İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS AND PROPERTIES OF AMINOSILANE-FUNCTIONALIZED URETHANE OIL/TITANIA HYBRID FILMS

M.Sc. Thesis by
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Department: Chemical Engineering

Programme: Chemical Engineering

JUNE 2009

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

AMİNOSİLAN İLE MODİFİYE EDİLMİŞ ÜRETAN YAĞI/TİTAN HİBRİT FİLMLERİ SENTEZLENMESİ VE ÖZELLİKLERİNİN İNCELENMESİ

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FOREWORD

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ABBREVIATIONS

AFUO	**:**	Aminosilane Functionalized Urethane Oil
APES	**:**	3-Aminopropyltriethoxysilane
$CDCl_3$	**:**	Chloroform
COU	**:**	Classic Urethane Oil
DCO	**:**	Dehydrated Castor Oils
DETA	**:**	Diethylenetriamine
DSC	**:**	Differential Scanning Calorimetry
FT-IR	**:**	Infrared Spectrophotometer
HDI	**:**	Hexamethylene Di-isocyanate
^{1}H-NMR	**:**	Nuclear Magnetic Resonance
IPTEOS	**:**	(3-isocyanatopropyl)triethoxysilane
$M(OR)_n$	**:**	Metal Alkoxides
MDI	**:**	Diphenyl Methane Di-isocyanate
MIC	**:**	Methyl Isocyanate
MSMA	**:**	(3-trimthoxysilyl)propyl Methacrylate
MTMS	**:**	Methyltrimethoxysilane
MWD	**:**	Molecular Weight Distribution
NDI	**:**	Naphthalene Di-isocyanate
P(MA-*co*-Itn)/TiO_2	**:**	Poly (Methyl Acrylate-*co*-Itaconic Anhydrate)/TiO_2
PG	**:**	Partial Glyceride
PMMA	**:**	Poly(methyl methacrylate)
PPG	**:**	Polypropylene Glycols
PPO	**:**	Polypropylene Oxide
RT	**:**	Room Temperature
TBOT	**:**	Tetrabutyl Titanate`
TCPTU	**:**	TiO_2-Triethoxysilane-Capped Polythiourethane
TDI	**:**	Toluene Diisocyanate
TEOS	**:**	Tetraethyl Orthosilicate
TGA	**:**	Thermogravimetric Analysis
THF	**:**	Tetrahydrofuran
TIP	**:**	Titanium Isopropoxide
TTIP	**:**	Titanium Tetra-Isopropoxide

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T_g	**:** Glass-transition temperature
nm	**:** Nanometer
µm	**:** Micrometer

SYNTHESIS AND PROPERTIES OF AMINOSILANE-FUNCTIONALIZED URETHANE OIL/TITANIA HYBRID FILMS

SUMMARY

Organic/inorganic hybrid materials posses advantages of organic polymers such as lightweight, flexibility, good impact resistance and good process ability as well as advantages of inorganic materials such as good chemical resistance, high thermal stability and high brittleness. Since these properties are expected from the coating materials, organic/inorganic hybrid composites are likely to have a great potential in coating applications.

Recently, polymer/titania hybrid materials were largely studied for their excellent thermal and optical properties. In the present study, titanium isopropoxide (TIP) based inorganic domain was combined with triglyceride oil together with alkoxysilane as a new material for oil based binder. For this propose, aminosilane-functionalized urethane oil (AFUO) was firstly synthesized by the reaction of 3-aminopropyltriethoxysilane (APES) and partial gyceride (PG) mixture with toluene diisocyanate. Then, this intermediate was combined with TIP by sol-gel reaction between alkoxy groups of AFUO and isopropoxide groups of TIP. This process was applied on the moisture saturated thin films on a glass plate. Then, the sol-gel procedure was completed by condensation reactions of Si−OH and Ti−OH groups.

Chemical bonding between titania domain and the polymer matrices was proved by FTIR. Film properties of the hybrid composite coating such as flexibility, adhesion, Sward Rocker hardness, water resistance, alkali resistance and acid resistance were determined according to the related standards. Additionally, thermal properties were determined by TGA and DSC analysis.

AMİNOSİLAN İLE MODİFİYE EDİLMİŞ ÜRETAN YAĞI/TİTAN HİBRİT FİLMLERİ SENTEZLENMESİ VE ÖZELLİKLERİNİN İNCELENMESİ

ÖZET

Organik ve inorganik hibrit malzemeler, organik polimerlerin hafifliği, esnekliği, darbe direnci ve kolay işlenebilirlik gibi özelliklerini taşımalarının yanı sıra, inorganik maddelerin kimyasallara karşı direnç, yüksek sıcaklık dayanımı, kırılganlık gibi avatajlarınıda bünyelerinde barındırırlar. Bu özelliklerin boya endüstrisinde aranan özellikler olmalarından dolayı organik/inorganik hibrit malzemeler boya endüstrisinde büyük ölçüde kullanım potansiyeline sahiptirler.

Mükemmel ısı ve optik özellikler taşımalarından dolayı polimer/titan malzemeler günümüzde geniş ölçüde çalışılmaktadır. Bu tezde, titanyum izopropoxide (TIP) temelli kısım alkoxysilan ile birlikte trigliserit yapısına bağlanarak yeni bir yağ bazlı bağlayıcı sentezlenmiştir. Bu amaçla ilk önce 3-aminopropiltrietoxysilan (APES)' ın kısmi gliserit ve toluen diisosiyanat varlığındaki reaksiyonundan alkoxysilan ile modifiye edilmiş üretan yağı sentezlenir. Daha sonra yapıya TIP, AFUO' nun alkoxy gruplarının TIP' nın isopropoxide gruplarıyla verdiği sol-gel reaksiyonlarıyla katılır. Bu proses cam plaka üzerine neme doymuş ince filmlere uygulanır. Sol-gel prosesi Si−OH ve Ti−OH gruplarının kondenzasyon reaksiyonları ile tamamlanır.

Titan yapısının polimer matrisi ile reaksiyonu FTIR analizi ile ispatlanmıştır. Esneklik, yapışma, sertlik, su, asit ve baza dayanıklılık testleri ilgili standartlarda belirtildiği gibi yapılmıştır. Kaplamanın ısıl özellikleri TGA ve DSC analizleri ile incelenmiştir.Yapılan testlerinde görülmüştürki aminosilan ile modifiye edilmiş üretan yağı/titan hibrit filmleri klasik üretan yağı filmlerinden daha iyi film özellikleri göstermişlerdir.Özellikle bu hibrit filmler baza ve suya dayanıklılık yüksek dayanıklılık göstermişlerdir. Isı dayanımları da klasik üretan yağı filmlerine göre daha yüksektir.

1. INTRODUCTION

Organic/inorganic hybrid materials posses advantages of organic polymers such as lightweight, flexibility, good impact resistance and good process ability as well as advantages of inorganic materials such as good chemical resistance, high thermal stability and high brittleness. As these properties are also expected from the coating materials, organic/inorganic hybrid composites are widely used in coating applications [1-4].

One of the challenges in producing hybrid materials with high performance is to control phase separation between organic and inorganic domains. To overcome this difficulty, formation of hydrogen bonding or covalent bonding between the organic and inorganic network has been utilized. Concerning this, a number of researchers have used alkoxysilanes to retard phase separations by facilitating crosslink reactions. For example, Qin et al. prepared transparent poly (methyl acrylate-*co*-itaconic anhydrate)/TiO_2 [P(MA-*co*-Itn)/TiO_2] hybrid materials by using 3-aminopropyltriethoxysilane (APES) as a coupling agent [5]. It was reported that without APES, opaque hybrid material was obtained, and phase separation was observed.

The synthesis of polymer/titania materials through Si-O-Ti bonding mainly was carried out by sol-gel method [6-12]. In these studies, tetrabutyl titanate (TBOT), titanium tetra-isopropoxide (TTIP), titanium (IV) chloride, titanium (IV) n-butoxide were used as Ti sources, and (3-isocyanatopropyl)triethoxysilane (IPTEOS), (3-methacryloxypropyl)trimethoxysilane, methyltrimethoxysilane (MTMS), (3-trimthoxysilyl)propyl methacrylate (MSMA), 3-(isocyanatopropyl) triethoxysilane, tetraethyl orthosilicate (TEOS), 3-aminopropyl triethysilane were used as Si sources. For instance, Chen et al. produced poly(methyl silsesquioxane) (MSQ)-titania films from titanium n-butoxide and MTMS [8]. The results showed that the prepared films were very uniform with an amorphous nanoscale titania segment. In another study, Xiong et al. synthesized homogeneous organic-inorganic hybrid materials with

excellent thermal and optical performance by the mixing of (3-methacryloxypropyl)trimethoxysilane-capped acrylic resin with titanium n-butoxide [7]. Moreover, Lu et al. prepared hybrid optical films of TiO_2-triethoxysilane-capped polythiourethane (TCPTU) with high refractive indices by titanium butoxide as titania precursor and IPTEOS as Si source [6].

In this study, aminosilane funtionalized urethane oil-titania hybrid coatings were prepared. Oil-modified organo-soluble polyurethanes, urethane oils, have been widely used as an organic coating since utilization of renewable sources in various industrial applications has become an important aspect in respect of the environmental and economic concerns. Urethane oils are produced via the reaction of diisocyanates with hydroxyl-containing oil or oil derivatives [13, 14]. Linseed, sunflower, safflower, soybean, tall and dehydrated castor oils (DCO) are among the oils used in the formulation of urethane oils. A number of reports have been appeared in the literature on the modification of oil component to improve the properties of the coatings [15-18]. Several studies have been carried out on urethane oils in our laboratory as well. In these studies, *Ecballium elaterium* and *Prunus Mahaleb L.* seed oils were used in the formulation of urethane oils [19]. In another study, the effect of the amount and the type of isocyanate component on the film properties of the final product was investigated [20]. In addition to these studies, the flow behavior of some urethane oils prepared at different reactant ratios was determined as well as the flow properties of some mixture prepared from urethane oil and alkyd resin (AR-UO) [21, 22].

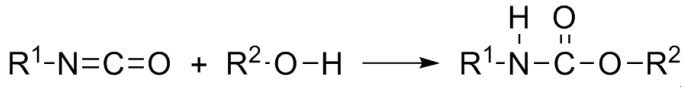
As mentioned above in the present study, aminosilane funtionalized urethane oil-titania hybrid coatings were prepared with TIP as the inorganic precursor to react with amionosilane functionalized urethane oil by sol-gel technique. The structure and thermal properties of the hybrid materials were studied by FTIR, ,TGA and DSC. Film properties such as flexibility [23], adhesion [24], Sward Rocker hardness [25], water resistance [26], alkali resistance [26] and acid resistance [26] were also determined according to the related standards.

2. THEORETICAL PART

2.1 Urethane Chemistry

2.1.1 Introduction

Polyurethanes are produced by the polyaddition reaction of a polyisocyanate with a polyalcohol (polyol). Generalized urethane reaction is given in Equation 2.1.



(2.1)

Carbamate (urethane) linkage, produced by reacting an isocyanate group, -N=C=O with a hydroxyl (alcohol) group, -OH is given in Figure 2. 1.

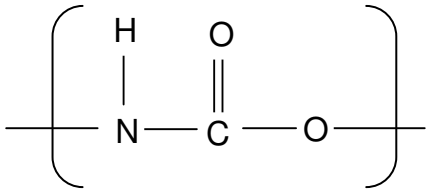


Figure 2.1 : Urethane linkage

Polyurethane polymers are formed through step-growth polymerization by reacting a monomer containing at least two isocyanate functional groups with another monomer containing at least two alcohol groups in the presence of a catalyst.

In the typical polyurethane synthesis, required amount of isocyanate, determined by the hydroxyl content of the polyol, is slowly added to the polyol at low temperature under stirring. Then, the reaction temperature is raised to 65-125 ^{o}C.

Urethanes are composed of soft and hard segments. For that reason, they can be considered as block copolymers. The soft segment has a low glass transition temperature(Tg) and a molecular weight around 400-5000 g/mol. Polyol is the soft segment of urethane and gives elastomeric properties to the polymer. On the other

hand, isocyantes are the hard segments of urethanes and they have high glass transition temperatures. The structure–property relations of polyurethanes are extremely diverse and easily controlled. Distribution of soft and hard segments play a crucial role in the modification of the physical and mechanical properties of polyurethanes. By changing the phase distribution of the hard and soft segments, properties can be adjusted for industry demands.

Isocyanates, polyols and chain extenders are the main components utilized in the synthesis of urethanes. The physical and chemical character, structure, and molecular size of these compounds influence final physical properties of the finished polyurethane. Besides these components, additive such as catalysts, surfactants, blowing agents, cross linkers, flame retardants, light stabilizers, and fillers are used to control and modify the reaction process and performance characteristics of the polymer.

2.1.2 Isocyanates

Isocyanates are organic compounds; aromatic and aliphatic, containing the isocyanate group–NCO. An isocyanate may have more than one isocyanate group. An isocyanate that has two isocyanate groups is known as a diisocyanate.

The isocyanate group reacts with the hydroxyl functional group to form a urethane linkage. If a diisocyanate is reacted with a compound containing two or more hydroxyl groups (a polyol), long polymer chains are formed, known as polyurethanes. The isocyanate group also reacts with the amine functional group. Reaction between a diisocyanate and a compound containing two or more amine groups, produces long polymer chains known as polyurethanes.

The most widely used industrial isocyanates are toluene di-isocyanate (TDI), diphenyl methane di-isocyanate (MDI), hexamethylene di-isocyanate (HDI), naphthalene di-isocyanate (NDI), methyl isocyanate (MIC). Chemical structures of these commonly used industrial isocyanates are given in Figure 2.2.

Isocyanates are divided into mono- and di-isocyanates. The monoisocyanates are subdivided into alkyl and aryl isocyanates; unsaturated isocyanates; halogenated alkyl and aryl isocyanates; carbonyl, thiocarbonyl and imidoyl isocyanates; sulfur isocyanates; phosphorus isocyanates; and inorganic isocyanates. The diisocyanates

are also divided into aliphatic and aromatic diisocyanates [13]. The aromatic polyisocyanates are significantly less expensive than the aliphatic types. This is due to the larger production volumes of the aromatic materials that find use in foams and other structural applications.

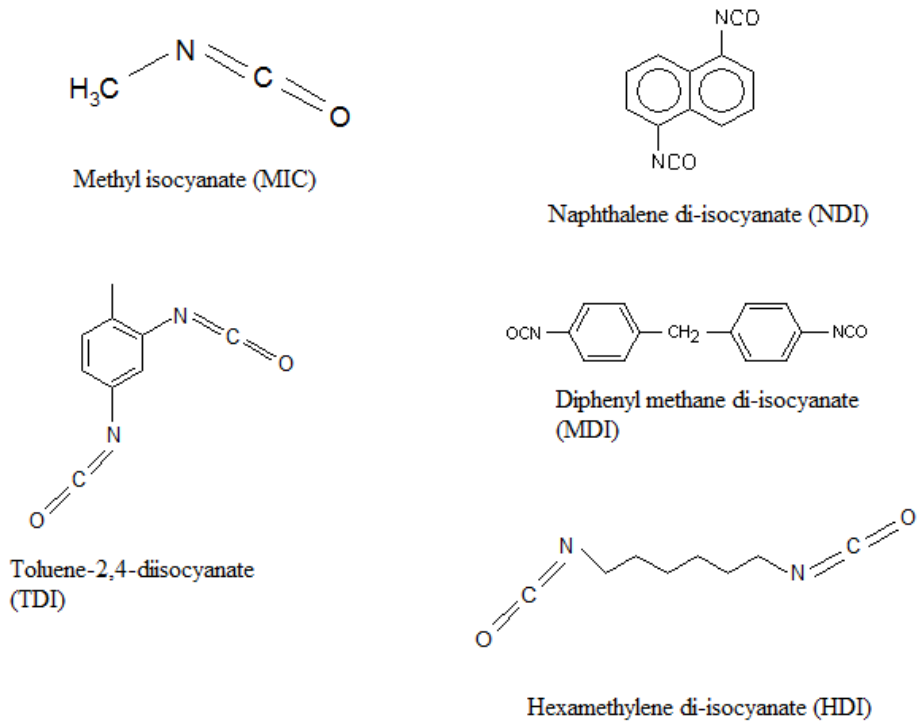
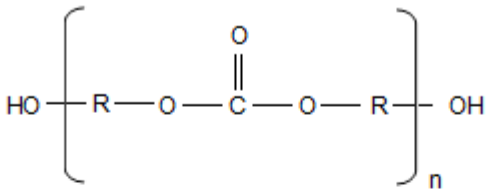


Figure 2.2 : Most widely used industrial isocyanates

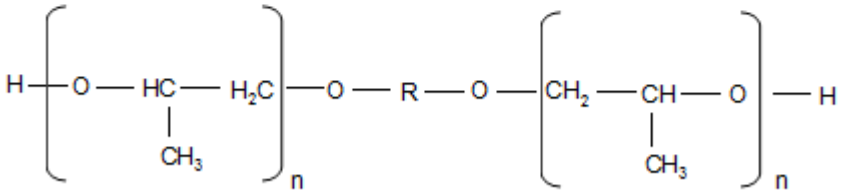
2.1.3 Polyols

Polyols used in polyurethane production can be divided into two groups in respect to their structure. In the first group there are the low molecular weight polyols, such as propylene glycol, ethylene glycol, dipropylene glycol, diethylene glycol, 1,4 butanediol, neopentyl glycol, triethanolamine, glycerol, etc. Polyether polyols (polypropylene glycols and triols) having molecular weights between 400 and 10,000 g/mol dominate in the foam technology. Polypropylene oxide (PPO) polyols, also called polypropylene glycols (PPG), are cheaper than other polyols. Due to the weak intermolecular attractive forces (low polarity) and non-crystallizing nature, PPG polyols are liquid at room temperature even at very high molecular weight, unlike polyester polyols, which are often crystalline greases.

Polyester polyols are an important class of urethane raw materials, with applications in elastomers, adhesives, etc. They are usually made from adipic acid and ethylene glycols (polyethylene adipate) or butane diol and adipic acid. Chemical structure of polyester polyols and polypropylene glycols are given in Figure 2.3.



polyester polyol



Polypropylene glycols

Figure 2.3 : Chemical structure of polyester polyols and polypropylene glycols

The second group of polyols for polyurethane contains low MW polymers with terminal hydroxyl groups called oligo-polyols, characterized by an average molecular weight and having a molecular weight distribution (MWD) of homologous species. An oligo-polyol for polyurethanes, may have two, three, four, five, six, seven or a maximum of eight hydroxyl groups/mol. Polyols with a higher number of hydroxyl groups/mol are rarely used (for example dendritic polyols) [27]. General formula of oligo-polyols is given in Figure 2.4.

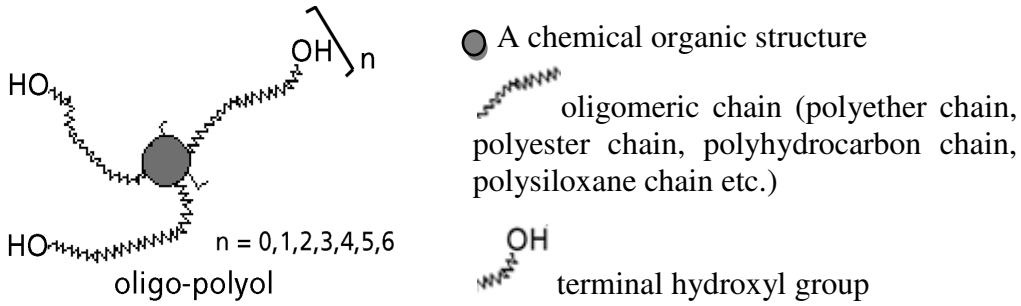


Figure 2.4 : General formula of oligo-polyols

2.1.4 Polyurethane Applications

Dr Otto Bayer synthesized the first polyurethane in 1937 by the reaction of a polyester diol with a diidocyanate at IG Farbenindustrie (Germany). This new reaction of synthesis of polymers called polyaddition reaction [27]. Since then, polyurethanes became one of the most dynamic groups of polymers , and their use covers practically all the fields of polymer applications. For example, foams, elastomers, thermoplastics, thermorigids, adhesives, coatings, sealants, fibres and so on. The following chart illustrates the product types and end uses for polyurethane chemicals (see Figure 2.5).

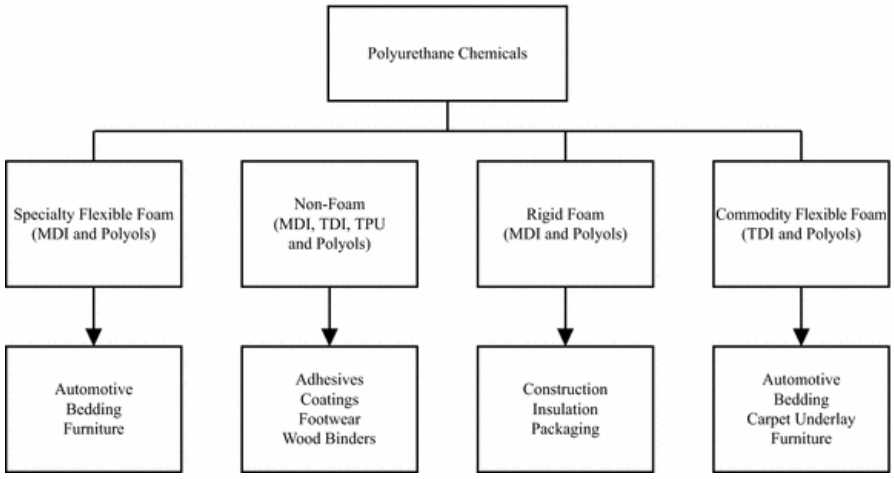


Figure 2.5 : Product types and end uses for polyurethane chemicals

Utilization of polyurethanes in different industries is the following: about 40% of PU is used in the furniture industry, 16% in transport, 13% in construction, 7% in refrigeration and about the same in coatings, 6% in the textile industry, 4% in the

footwear industry and 8% for other applications. The main applications of polyurethanes are presented in Figure 2. 6 [28].

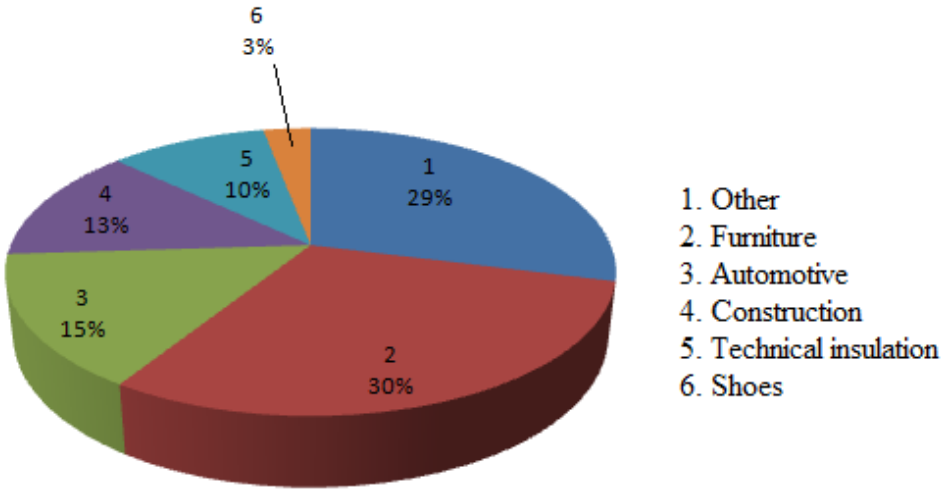


Figure 2.6 : The main applications of polyurethanes

2.2 Triglyceride Oils

2.2.1 Introduction to triglyceride oils

Triglycerides are formed from a single molecule of glycerol, combined with three fatty acids on each of the OH groups. Ester bonds form between each fatty acid and the glycerol molecule. Fatty acids are mainly even-numbered, straight-chain, aliphatic (saturated or unsaturated) monocarboxylic acids with chains ranging from C_4 to C_{24}. Fatty acids vary in unsaturation ranging from total saturation to 1, 2, 3 or 4 double bonds [29]. Structure of a triglyceride molecule is given in Figure 2.7. Triglycerides compose of sites which are able to undergo chemical reactions. These sites are the double bond, the allylic carbons, the ester group, and the carbons alpha to the ester group.

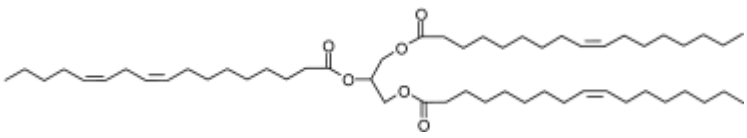


Figure 2.7 : A triglyceride molecule

Polymers produced from the modified triglycerides have been widely used as coatings, inks, paints and polyurethane foams mostly. However, in some applications modified triglycerides were used to produce toughening agents and polyurethane foams and so on. Nevertheless, plant oils with their original forms, cannot be used to produce polymers except castor oil. One of the ways to modified triglyceride oils is the glycerolysis reaction. Glycerolysis is a special case of transesterification. The final product is mostly the mixture of mono and digycerides and found application commonly as coatings. For coating applications, double bonds in mono glycerides are reacted to form the coating. In addition to this application, monoglycerides can also react with comonomers such as diacids, epoxies, anhydrides, or isocyanates by polycondensation reactions.

As another method, triglyceride oils derived from plants have been used to synthesize several different monomers for use in structural applications. These monomers have been found to form polymers with a wide range of physical properties. This method is to modify triglycerides by employing hydroxylation reaction followed by glycerolysis reaction. With this method, monoglycerides will be produced from triglycerides [30].

In addition to the advantage of process ability, triglycerides are able to be broken down readily by lipase enzymes. Which means that economic and environmental friendly biodegradable polymers can be produced from triglycerides.

2.2.2 Oxidation of triglycerides

Oxidation is the chemical reaction of an oil molecule with oxygen, which is present from either ambient or entrained air. The mechanism of autoxidation of vegetable oils is classically regarded as following a number of stages [31]:

1) a (usually slow) initiation phase
2) a (rapid) propagation phase
3) and a termination phase.

The initiation phase involves the formation of a free radical from a triglyceride molecule in the fat – this may be promoted by the presence of heavy metals in the oil, or by heat or light. The next stage is the reaction of the triglyceride free radical with

oxygen to produce a peroxide free radical, which can react with another triglyceride to produce a hydroperoxide and another triglyceride free radical. Steps 2 and 3 can repeat in a chain reaction until two peroxy free radicals collide and neutralize each other. Steps of oxidation mechanism is given in the following reactions.

$$RH \longrightarrow R\cdot + H\cdot \quad \textbf{(2.2)}$$

(triglyceride ⟶ triglyceride free radical plus hydrogen free radical)

$$R\cdot + O_2 \longrightarrow ROO\cdot \quad \textbf{(2.3)}$$

(triglyceride free radical plus oxygen ⟶ peroxy free radical)

$$ROO\cdot + RH \longrightarrow R\cdot + ROOH \quad \textbf{(2.4)}$$

(peroxy free radical plus triglyceride ⟶ triglyceride free radical)

Drying properties of oils is indicated by their iodine numbers. Iodine number is a measure of the unsaturation of fats and oils. Express in terms of the number of centigrams of iodine absorbed per gram of sample (percentage by weight of iodine absorbed).Oils with an iodine number lower than 120 g/100 g of oil called as non-drying oils such as castor oil and coconut oil. Oils gives an iodine number between 120-150 g/100 g of oil refer to as semi-drying oils such as soybean, sunflower, safflower, and tall oil. On the other hand, oils have an iodine number higher than 150 g/100 g of oil considered as drying oils such as tung, oiticica, linseed, and perilla.

2.3 Sol-Gel Process

2.3.1 Introduction

A sol is a colloidal suspension in which the dispersed phase is so small (~1-1000 nm) that gravitational forces are negligible and interactions are dominated by short-range forces, such as van der Waals attraction and surface charges. A gel is a porous 3-dimentally interconnected solid network that expands in a stable fashion throughout a liquid medium and is only limited by the size of the container. If the solid network is made of colloidal sol particles the gel is said to be colloidal. A sol-gel process is a colloidal route used to synthesize ceramics with an intermediate stage including a sol and/or a gel stage [32]. An overview of the sol-gel process is presented in Figure 2.8.

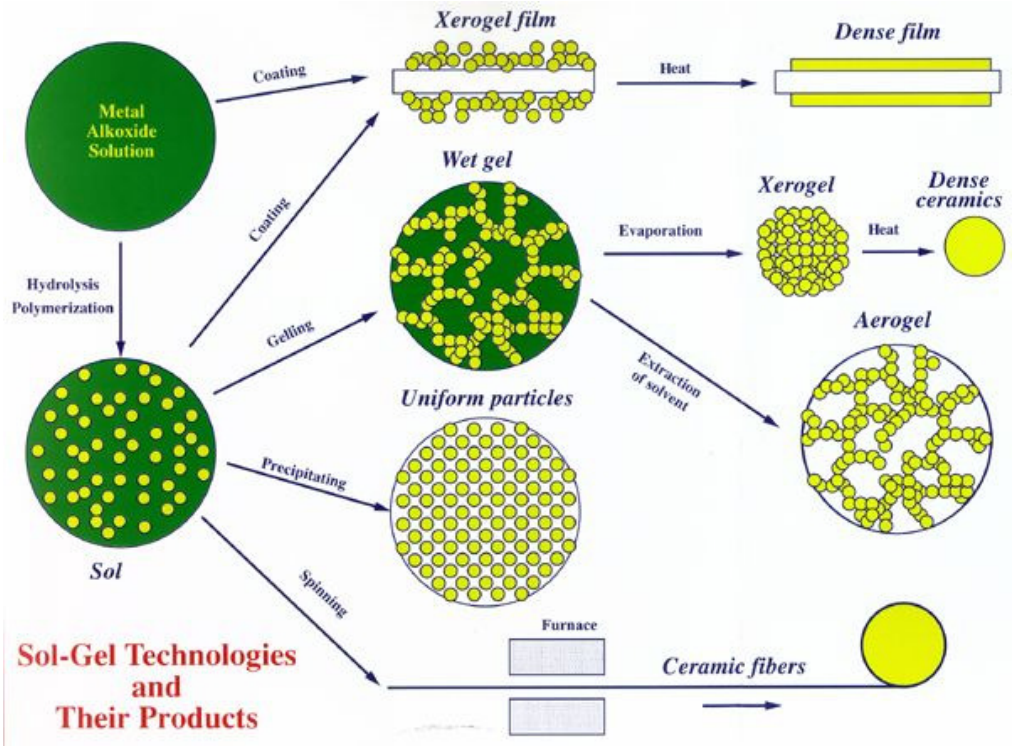


Figure 2.8 : Overview of the sol-gel process

In the sol-gel process, starting compounds, the precursor for preparation of a colloid consist of a metal or metalloid element surrounded by various *ligands*. Metal alkoxides, $M(OR)_n$, are derivatives of alcohols, are common precursors since they can react easily with water. Sol-gel processes occur in two steps. First step is the hydrolysis reactions in which a hydroxyl ion becomes attached to the metal atom, as shown in the following reaction.

$$Si{-}(OR)_4 + H_2O \rightarrow HO{-}Si(OR)_3 + ROH \qquad \textbf{(2.5)}$$

The metal may partially or completely hydrolyze depending on the amount of water or presence of catalyst. When the hydrolysis reaction reach completion, the following reaction occurs.

$$Si{-}(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH \qquad \textbf{(2.6)}$$

In the second step of sol-gel processes, two partially hydrolyzed molecules link together in a condensation reaction with the elimination of water or alcohol.

$$(OR)_3Si{-}OH + HO{-}Si(OR)_3 \rightarrow (OR)_3Si{-}O{-}Si(OR)_3 + H_2O \quad \textbf{(2.7)}$$

$$(OR)_3Si{-}OR + HO{-}Si(OR)_3 \rightarrow (OR)_3Si{-}O{-}Si(OR)_3 + ROH \quad \textbf{(2.8)}$$

Elimination of water gives an extended silica gel matrix (known as a xerogel when dry). If desired, residual Si–OH groups remaining in the xerogel product can be removed at elevated temperature to give fully densified SiO_2. Also, mixtures of different precursor compounds can undergo sol-gel conversion to give gels of complex composition.

All reactions are catalyzed, typically by the presence of an acidic or alkaline medium. The nature of the catalyst and, in particular, the pH of the reaction have a very pronounced effect on the hydrolysis and condensation reactions and the structure of the inorganic network formed. In brief, the presence of acid tends to produce more linear or polymer like molecules in the initial stages because the rate of hydrolysis is high relative to the rate of condensation. This will result in the formation of high-density, low fractal dimension structures. In contrast, a basic environment tends to produce more of a cluster growth leading to dense, colloidal particulate structures due to the high condensation rate.

Sol-gel reactions are the key reactions in the preparation of inorganic/organic composite materials. On the basis of the molecular structure of inorganic and organic components, the connection between inorganic and organic phases, and the preparation technique, the inorganic/organic composite materials prepared by the sol-gel process can be divided into several groups. These groups are inorganic/organic composite materials incorporated through with or without covalent bonding, incorporation of small organic molecules, in situ formation of inorganic species within a polymeric network, interpenetrating networks and simultaneous formation of inorganic and organic phases.

2.3.2 Applications of sol-gel process

The combination of different materials for achieving novel properties has been of great interest because the properties of the primary materials do not always meet the requirements for a specific application. A new class of composite materials has been developed in recent years through the combination of inorganic metal alkoxides and low molecular weight organics and polymers (often functionalized) by the sol-gel approach [33, 34]. Unlike the traditional composite materials, which have macroscale domain size of micron and even millimeter scale, many of these new inorganic/organic composites are nanoscopic, with the physical constraint of several nanometers as the minimum size of the components or phases. The term "nanocomposite" is also used by some researchers. As a result of this nanoscale domain size, these inorganic/organic composite materials may possess properties that the traditional composite materials do not have, such as optical transparency. Through the combinations of different inorganic and organic components, different types of primary and secondary bonding, and different processing methods, materials with new properties can be produced for electrical, optical, structural, or related applications. The inorganic/organic composite materials made in this way, which have also been termed "ceramers" by Wilkes et al. and "ormosils" by Schmidt, are of considerable interest because of their potential for providing unique combinations of properties that cannot be achieved by conventional methods [35,36]. For example, the brittleness, optical, and nonlinear optical characteristics of glasses can be greatly modified by incorporating organic materials into the inorganic network.

2.3.3 Sol-gel process in coating applications

The sol-gel process has been extensively applied in the preparation of coating materials because the shrinkage problem in the preparation of monolithic materials by the sol-gel process can be avoided. Sol-gel coatings made from metal alkoxide already have commercial applications for glass and metal substrates. However, the applications of these pure metal alkoxide sol-gel coatings encounter some difficulties, especially for polymeric substrates. One problem is the crack formation associated with the shrinkage during the drying process. As a result, thick coatings are difficult to obtain. Another problem is the poor adhesion between the coating and polymer substrate. All of these problems can be overcome by using

inorganic/organic composite as the coating materials. The introduction of organic/polymeric components into the inorganic network reduces the extent of shrinkage because less byproducts are produced. It also brings flexibility to the brittle inorganic network and, most importantly, increases the adhesion between the coating and polymer substrate. Schmidt has developed a series of scratch- and abrasive-resistant coating materials that are based on $A1_2O_3$, ZrO_2, TiO_2, or SiO_2 as network formers and epoxy or methacrylate groups bound to Si via a ≡Si-C bond [37, 38]. They can be thermally cured at low temperature and thus can be applied to organic polymers. Another series of abrasive-resistant hard coating materials that are based on organoalkoxysilanes (such as triethoxysilane functionalized DETA or glycerol) and metal alkoxides as the precursors of composite networks have also been developed by Wilkes and co-workers [39]. They have been applied on poly(methyl methacrylate) (PMMA), polycarbonate. The abrasion resistance of these coated polymers is improved substantially. These coatings can also be applied on inorganic glass and metal substrates. Because reactive organic groups can be introduced into the inorganic networks, other functional coating materials have also been studied. For example, fluorescent coatings can be made by the introduction of fluorescent organic dye [40]. High refractive index optical coatings can also be obtained [41].

3. EXPERIMENTAL WORK

3.1.Materials

Refined sunflower oil purchased from the market was used as received. Toluene diisocyanate (TDI, 98%, Aldrich), 3-Aminopropyltriethoxysilane (APES, 98%) and titanium (IV) isopropoxide (TIP) were purchased from Sigma-Aldrich and were used without further purification. Glycerin, sulfuric acid, Na_2SO_4, acetic anhydride, pridin, KOH, HCl (%37) were obtained from Merck and were used as obtained.

3.2. Equipment

3.2.1 Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra were recorded on a Perkin Elmer FTIR Spectrum One B spectrometer.

3.2.1 Nuclear magnetic resonance spectroscopy (^{1}H NMR)

Chemical structure of the polymers were also determined by using Bruker 250 MHz spectrometer. $CDCl_3$ was used as a solvent.

3.2.2 Thermal gravimetric analysis (TGA)

Perkin Elmer Diamond TG/DTA was used for TGA analysis. The measurements were done from RT to +1200 ºC with a heating rate of 20 ºC/min. The analysis was used to determine the solid content left when the polymer was heated up to 1200 ºC.

3.2.3 Differential scanning calorimeter (DSC)

The glass transition temperatures of the samples were determined by a Perkin Elmer Diamond Differential Scanning Calorimeter. The samples were first heated from 30 ºC to 100 ºC with a heating rate of 20 ºC/min. Then, after cooling down to - 60 ºC, samples were subjected to second heating from – 60 ºC to 200 ºC with a heating rate of 20 ºC/min. Glass transition temperatures of the samples were determined by using the second heating flow.

3.3. Preparation Methods

3.3.1. Preparation of partial glyceride

Partial glyceride was prepared by glycerolysis reaction between triglyceride oil and glycerol. Sunflower oil and glycerol (glycerol/oil, g/g:0.085) were placed into a reaction flask and heated. When the temperature reached 218 ºC, $Ca(OH)_2$ (0.1 weight % of the oil portion) was added as a catalyst. The temperature was then set at 230 ºC and maintained for 1 hour under nitrogen atmosphere. After cooling, the reaction mixture was dissolved in diethyl ether and washed first with dilute sulfuric acid and then with water in order to remove the catalyst and free glycerol. The etheral solution was dried over Na_2SO_4 and then the solvent was removed. Hydroxyl and acid values were determined as 122.5 mg KOH / g and 2.4 mg KOH /g, respectively [42]. The hydroxyl value is the number of mg. of potassium hydroxide required to neutralize the amount of acetic acid capable of combining by acetylation with 1g. of sample. For this determination acetic anhydride solution in prydine was used as acetylation agent.

3.3.2. Preparation of aminosilane – functionalized urethane oil (AFUO)

Partial glyceride mixture and 3-Aminopropyltriethoxysilane ([OH]:[NH_2]=1:1) were dissolved in toluene and then were taken into the reaction flask and heated. When the temperature was reached 40-50 ºC, TDI as equivalent amount to [NH_2] + [OH] was added drop wise over a 30 min period. Following this, the temperature was raised to 90-95 ºC and the reaction was maintained for 4 h under nitrogen atmosphere.

3.3.3. Moisture curing of AFUO

Samples of AFUO were thinned with toluene to 50% solid content. Lead naphthenate and cobalt naphthenate were added 1% and 0.1% as metal based on solid content, respectively. 24 hours after adding driers, AFUO samples were subjected to moisture curing. For this purpose, the film samples applied on a glass plate with a Bird film applicator of 40 µm thickness and were placed in a cabinet of 90 % humidity at ambient temperature. After 24 hours, the film samples were removed and placed into an oven at 100 ºC for 12 h to crosslink through condensation of Si-OH groups [43].

3.3.4. Preparation of classical urethane oil (CUO)

Classical urethane oil was prepared as a comparative sample. PG mixture was dissolved in toluene and heated to 40-50 ºC. An equivalent amount of TDI was added slowly over 30 min period. Lead naphthenate as a 24 wt. % solution in white spirit was added in the amount of 0.02 wt. % of the oil portion. Then the temperature was set at 90-95 ºC and the reaction maintained for 4 h under nitrogen atmosphere.

3.3.5. Preparation of AFUO/titania hybrid composite films

AFUO was prepared in toluene medium as explained above. Toluene was removed by rotary evaporator. TIP in THF was then added into AFUO and stirred for 20 min. The titania content was varied in the range of 5-20 wt % by changing the feed ratio of titania precursor [$Ti(OC_3H_7)_4$] to AFUO. Lead naphthenate and cobalt naphthenate were added 1% and 0.1% as metal based on solid content, respectively. This mixture were stirred for 24 h at room temperature. Following this, the film samples applied on a glass plate with a Bird film applicator of 40 µm thickness and were placed in a cabinet of 90 % humidity at ambient temperature. After 72 hours, the film samples were removed and placed into an oven at 100 ºC for 48 h to complete crosslinking.

3.3.6 Characterization

The structures of CUO as well as AFUO and TiO_2-AFUO hybrid materials were characterized by using Fourier-Transform Infrared Spectroscopy (Perkin Elmer FT-IR Spectrum One B spectrometer), and Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR, Bruker 250 MHz, $CDCl_3$). Thermal analysis were done by a Thermogravimetric Analyser (Perkin Elmer Diamond TG/DTA) and a Differential Scanning Calorimeter (Perkin Elmer Diamond DSC).

Film properties such as drying time [44], flexibility [23], adhesion [24], Sward Rocker hardness [25], water resistance [26], alkali resistance [26] and acid resistance [26] were determined. For this purpose, film samples of moisture cured AFUO and TiO_2-AFUO were directly used. CUO samples, on the other hand, were diluted to 60 % solid content and film properties were determined 24 h after adding lead naphthenate and cobalt naphthenate as 1% and 0.1% metal based on solid content, respectively. A Bird film applicator with a 40 µm aperture was used for film

application. Tin plate panels were employed as a substrate for flexibility and water resistance tests, while glass tubes were used for alkali and acid resistance tests, as explained in the related standard methods.

4. RESULTS AND DISCUSSIONS

4.1 Synthesis of AFUO

The aim of this study is to improve film properties of classical urethane oils. For this purpose, APES and TIP were inserted to the urethane oil structure. As mentioned before, APES was firstly combined to the urethane oil structure through the reaction between NH_2 groups of APES and –N=C=O groups of TDI. The representative structure of AFUO is shown in Figure 4.1.

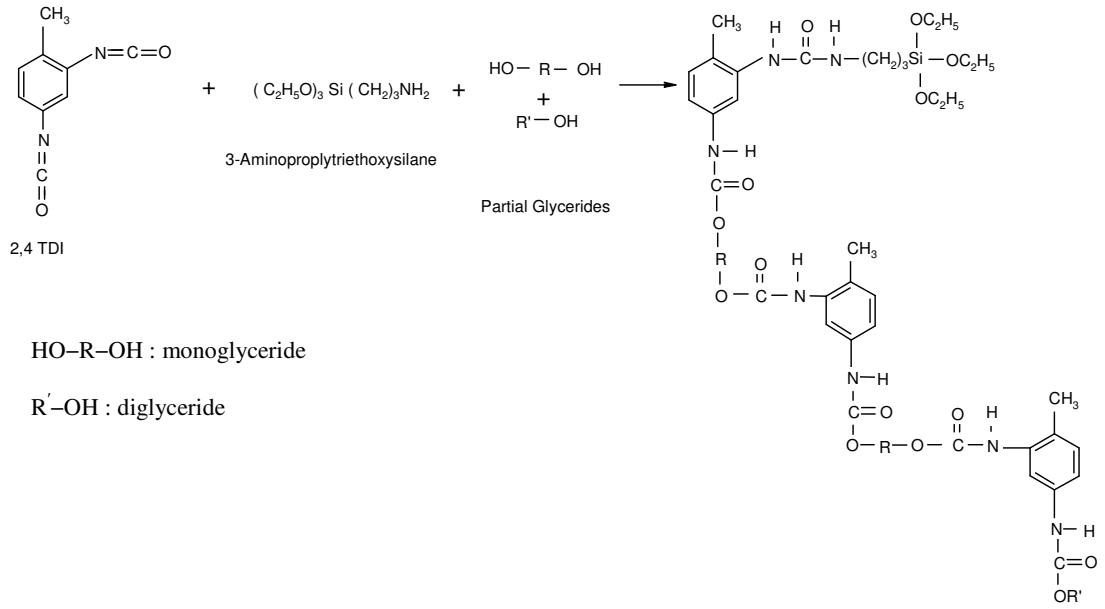


Figure 4.1 : Synthesis and representative structure of AFUO

Alkoxysilane modified urethane oil (AFUO) formation was monitored by FTIR as depicted in Figure 4.2. Disappearance of the free isocyanate peak at 2266 cm^{-1} shows that the reaction was completed after 4h at applied conditions.

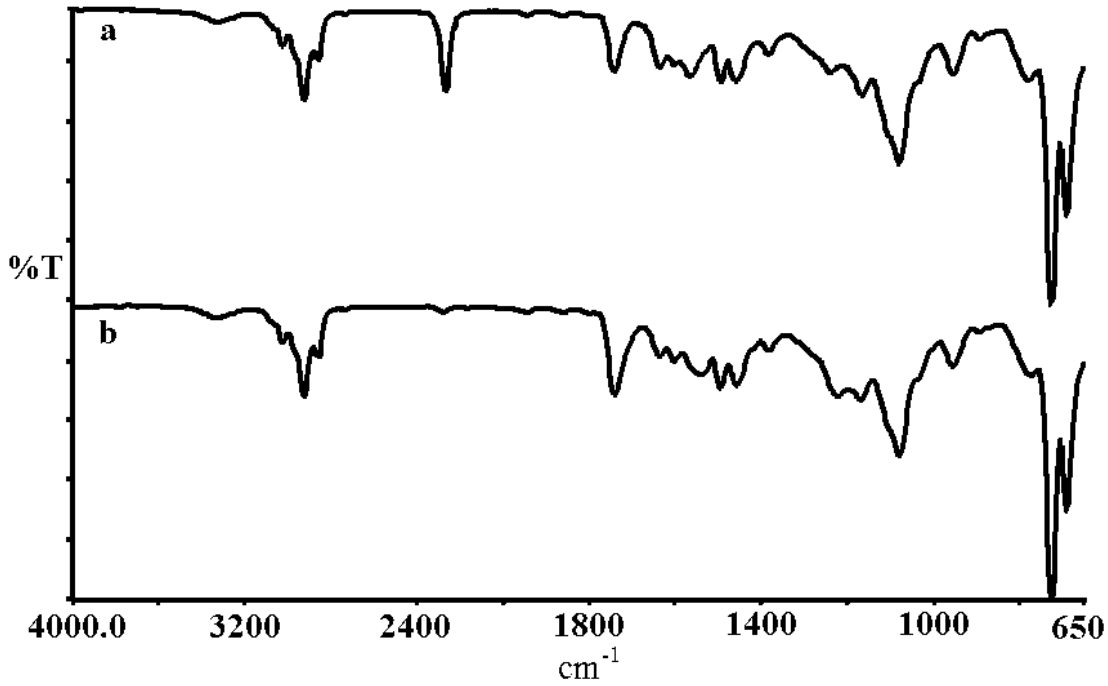


Figure. 4.2 : Monitoring of the AFUO formation by FTIR: (a) at the beginning of the reaction, (b) after 4 h reaction.

Figure 4.3 shows the ^{1}H NMR spectra of AFUO and CUO. The peaks at 0.691ppm (−C<u>H</u>$_2$−Si−), 1.23 ppm (−Si−O−CH$_2$−C<u>H</u>$_3$), 3.12 ppm (−NH−C<u>H</u>$_2$−CH$_2$−CH$_2$−Si−) and 3.79 ppm (−Si−O−C<u>H</u>$_2$−CH$_3$) indicate the incorporation of APES into the urethane oil structure [43, 45].

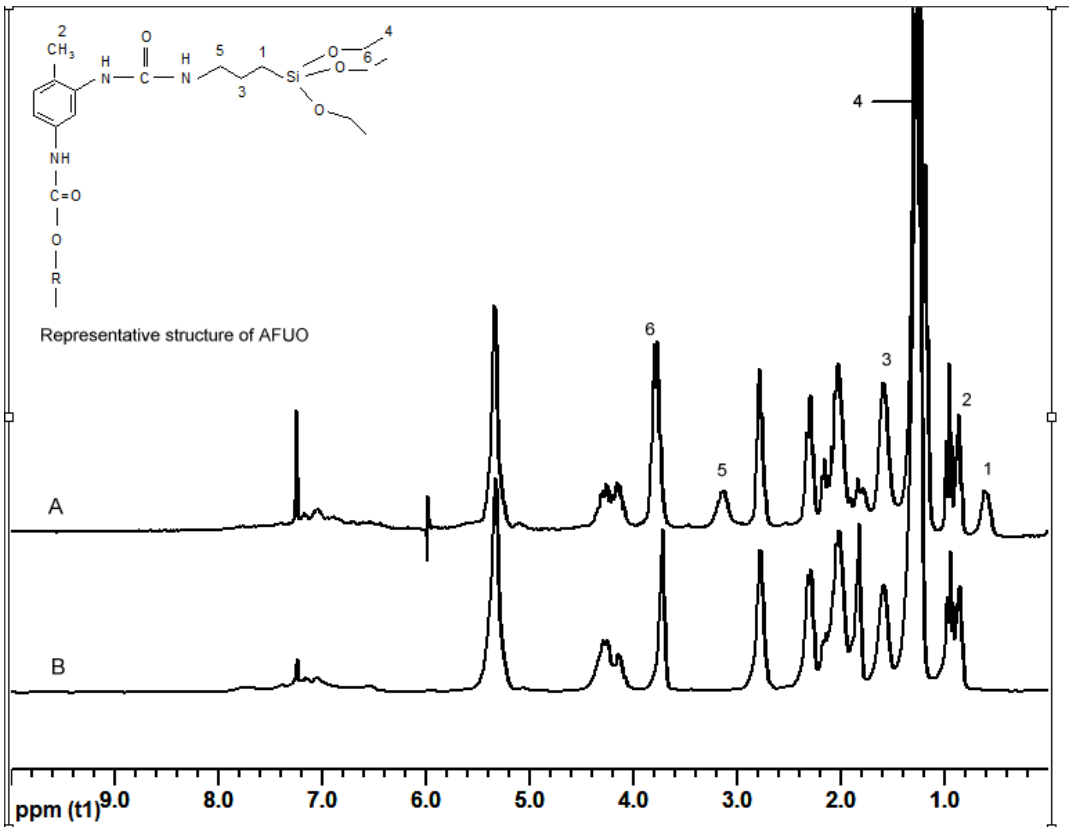


Figure 4.3 : ^{1}H-NMR spectrums of (a) AFUO and (b) CUO

4.2 Moisture Curing of AFUO

In order to determine film properties, moisture curing process was applied as explained in the experimental part. In this process, hydrolysis and condensation reactions take place yielding a crosslink structure. Reactions of the moisture-curing process are depicted in the equation 4.1 to 4.3. In the first step, the alkoxy group of APES absorbs moisture to form a silanol and an alcohol. Then, in the second step, condensation reaction between silanol groups occur by the elimination of water. A silanol may also react with an alkoxy group and give an alcohol.

$$\equiv Si{-}OR + H_2O \rightarrow \equiv Si{-}OH + ROH \quad \textbf{(4.1)}$$

$$\equiv Si{-}OH + \equiv Si{-}OH \rightarrow \equiv Si{-}O{-}Si\equiv + H_2O \quad \textbf{(4.2)}$$

$$\equiv Si{-}OR + \equiv Si{-}OH \rightarrow \equiv Si{-}O{-}Si\equiv + ROH \quad \textbf{(4.3)}$$

During this process, surface hydroxyl groups of the substrate can involve in the condensation reactions, causing a good adhesion to the surface. Interactions between aminosilane functionalized urethane oil and a hydroxyl containing substrate is given in Figure 4.4.

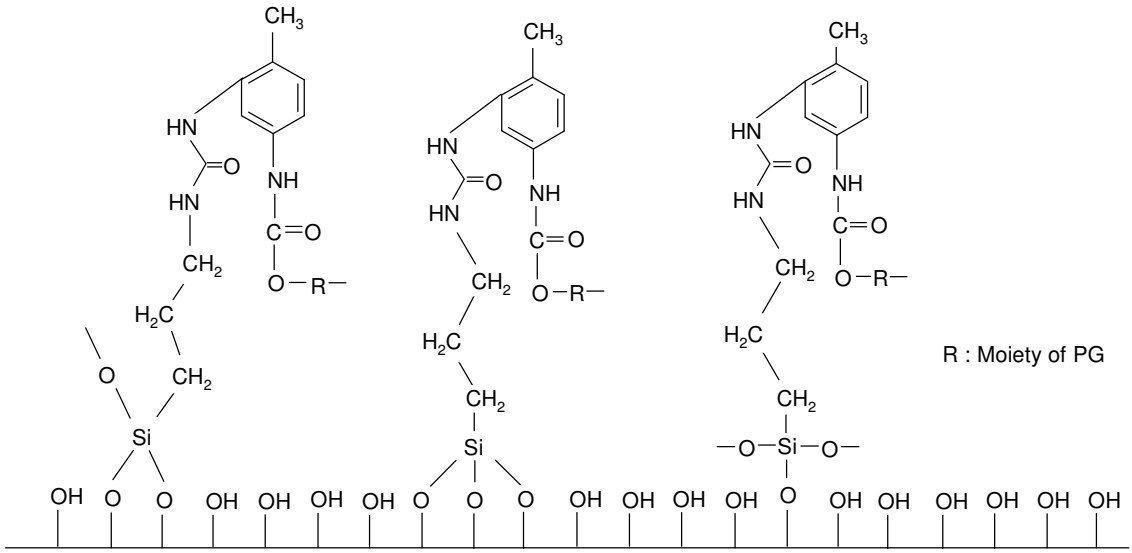


Figure 4.4 : Representative interaction between coating film and glass substrate

FTIR spectrums of AFUO before and after moisture curing and air dried CUO film samples are showed in Figure 4.5. The peak in 1000-1200 cm^{-1} region is wider for moisture cured AFUO film samples compared to CUO. This wider peak is assigned to the overlapping of the peaks corresponding to —Si—O—Si—, —C—Si—O— and —Si—O—C— stretching [43]. In addition, disappearance of the peak corresponding to Si—O stretching vibrations (955 cm^{-1}, Si-OCH_2CH_3) after moisture curing shows that the crosslinking was achieved in the moisture curing process.

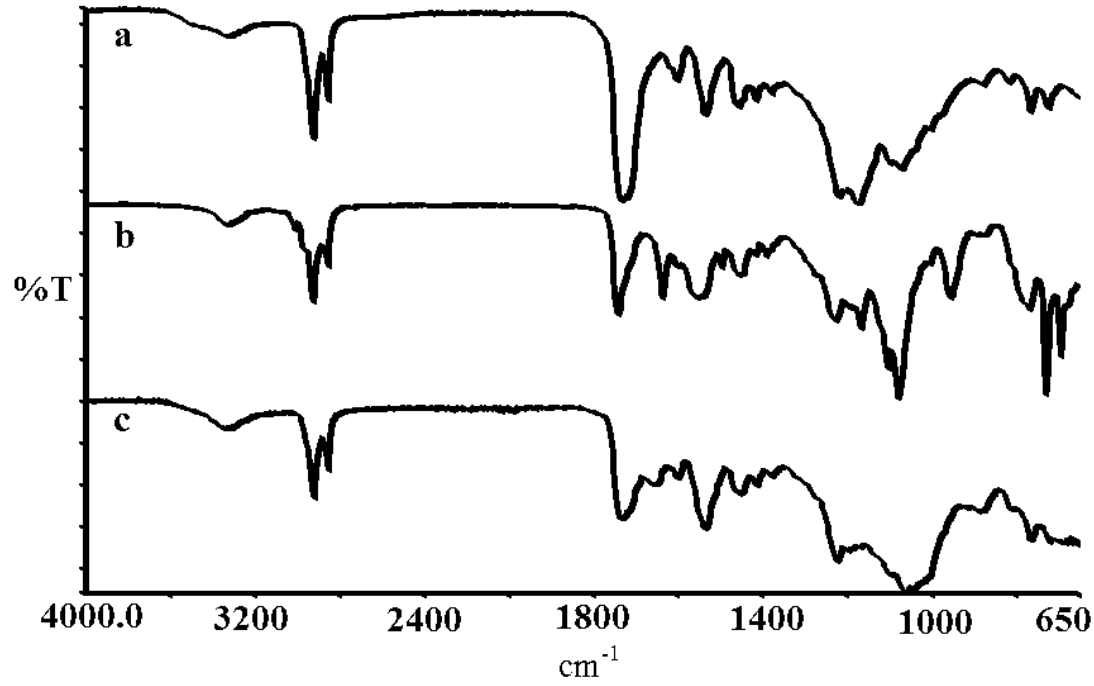


Figure 4.5 : IR spectra of (a) air dried CUO film, (b) AFUO before moisture curing and (c) moisture cured AFUO film.

4.3 Synthesis of AFUO/titania Hybrid Films

TIP was combined with AFUO structure in order to investigate effects of titania domain on the properties of the film samples. The representative structure of AFUO/titania hybrid material is given in Figure 4.6.

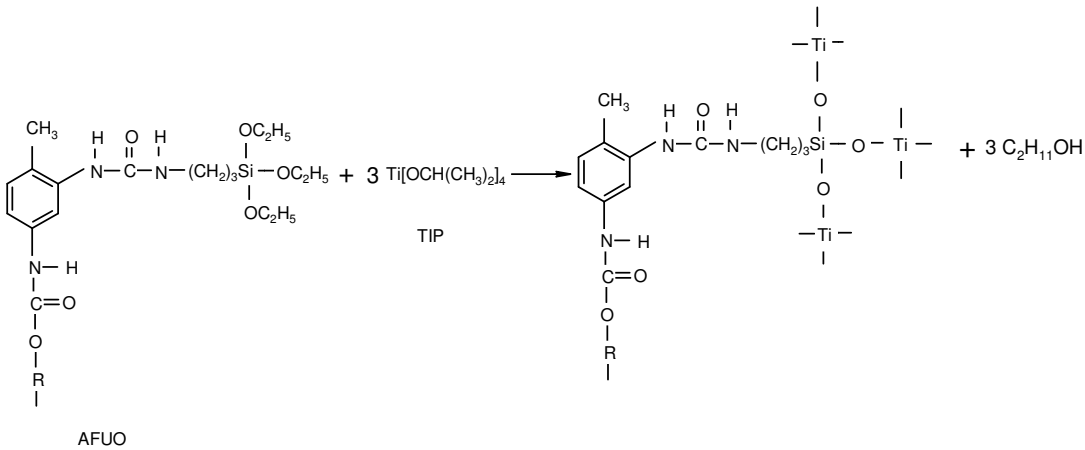


Figure 4.6 : Synthesis and representative structure of AFUO/titania hybrid material

Titania inorganic part was inserted by the sol-gel reactions between alkoxy groups of the AFUO and isopropoxide groups of TIP. Possible hydrolysis and condensation reactions of isopropoxide groups of titania precursor [$Ti(OC_3H_7)_4$] are given as in the following equations.

$$\equiv Ti{-}OR + H_2O \rightarrow \equiv Ti{-}OH + ROH \quad \textbf{(4.4)}$$

$$\equiv Ti{-}OH + \equiv Si{-}OH \rightarrow \equiv Ti{-}O{-}Si\equiv + H_2O \quad \textbf{(4.5)}$$

$$\equiv Ti{-}OH + \equiv Ti{-}OH \rightarrow \equiv Ti{-}O{-}Ti\equiv + H_2O \quad \textbf{(4.6)}$$

$$\equiv Ti{-}OH + \equiv Ti{-}OR \rightarrow \equiv Ti{-}O{-}Ti\equiv + ROH \quad \textbf{(4.7)}$$

Figure 4.7 shows the FTIR spectrum of TiO_2-AFUO hybrid films prepared by using TIP in the range of 5-20 wt %. The absorption band at around 900 cm^{-1} corresponds to Si–O–Ti stretching bond [6, 11]. The broad peak in the region of 1000-1200 cm^{-1} is assigned to the overlapping of the peaks corresponding to —Si—O—Si—, —C—Si—O— and —Si—O—C— stretching [43].

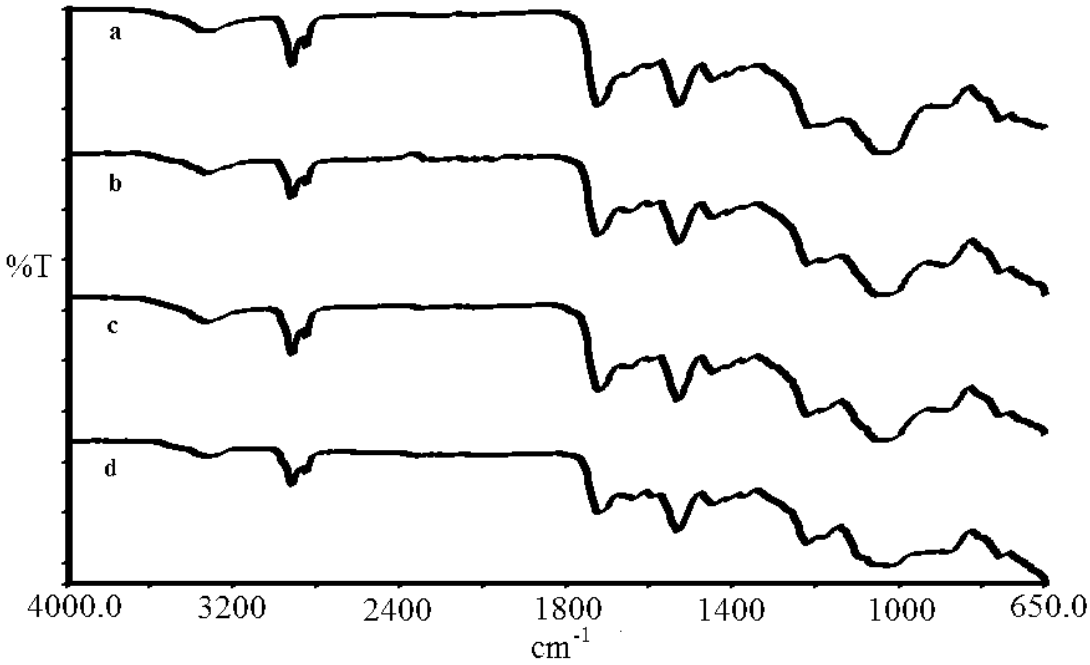


Figure 4.7 : FTIR spectrum of AFUO/titania hybrid films prepared by using (a) 5, (b) 10, (c) 15, (d) 20 wt. % of TIP.

4.4 Thermogravimetric Analysis (TGA)

4.4.1 Thermogravimetric analysis of moisture cured AFUO

Thermogravimetric analysis of moisture cured AFUO and air dried CUO film samples were carried out and compared as seen in Figure 4.8. Moisture cured AFUO lost 81 % of its original weight at 600 °C whereas air dried CUO lost 88 %. This suggests that due to its crosslink structure, moisture cured AFUO exhibits better thermal stability than air dried CUO.

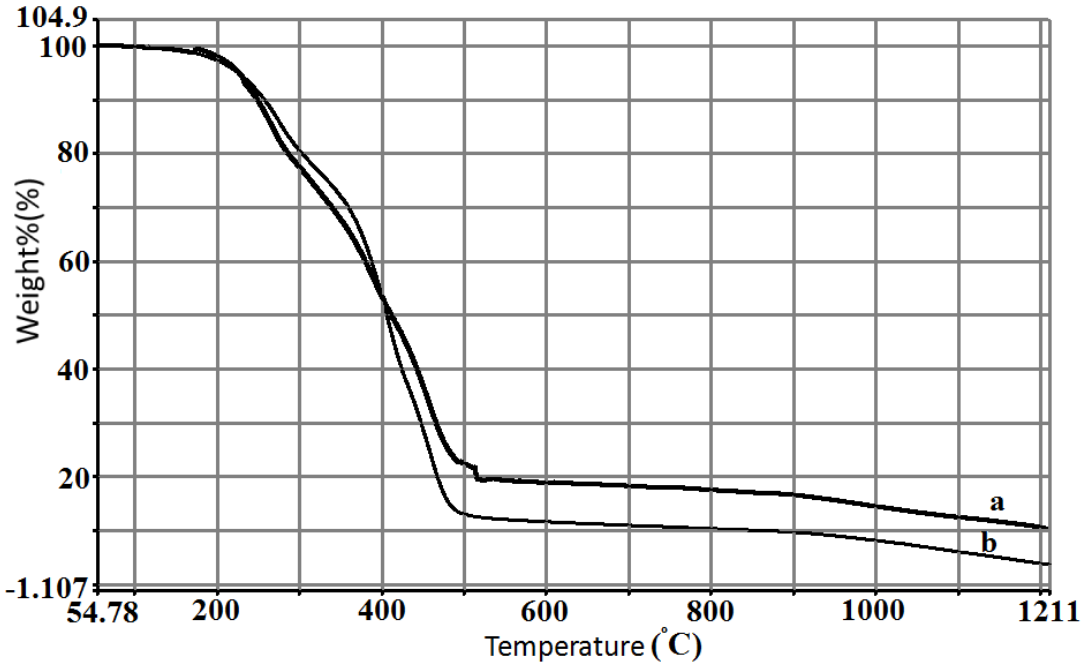


Figure 4.8 : TGA curves of (a) moisture cured AFUO and (b) air dried CUO film samples

4.4.2 Thermogravimetric analysis of AFUO/titania hybrid films

Figure 4.9 shows TGA curves of AFUO/titania hybrid films prepared by using TIP in the range of 5-20 wt % and Table 4.1 indicates weight % lost of the hybrid films at 900 °C. As seen from TGA data that the thermal stability of AFUO/titania hybrid films was improved by the addition of TIP. AFUO/titania hybrid film containing 20 wt. % of TIP exhibits the highest thermal stability.

Table 4.1 : Weight % lost for AFUO/titania hybrid films at 900 °C.

Samples (wt. % of TIP)	Weight % Lost
5	90.4
10	80.8
15	77.1
20	74.5

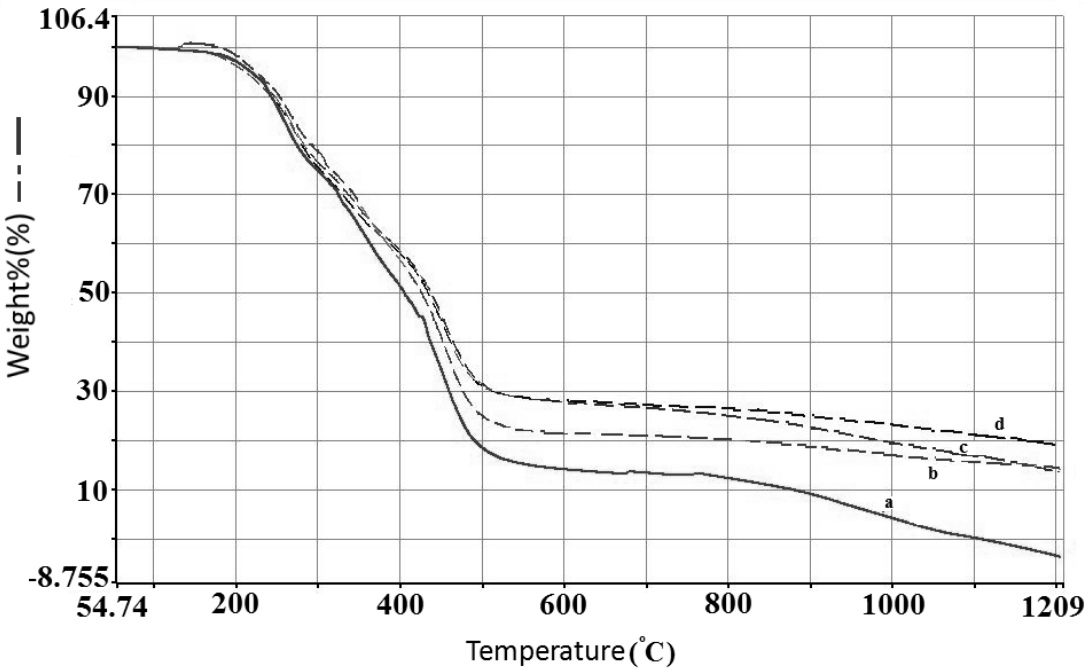


Figure 4.9 : TGA curves of AFUO/titania hybrid films prepared by using (a) 5, (b) 10, (c) 15 and (d) 20 wt. % of TIP.

4.5 Differential Scanning Calorimeter (DSC)

4.5.1 Differential scanning calorimeter of moisture cured AFUO

Figure 4.10 and Figure 4.11 show DSC curves of moisture cured AFUO and air dried CUO, respectively. As seen from Figure 4.11, air dried CUO exhibits a glass transition temperature (Tg) of about -7.59 °C. However, no significant thermal transition points below 200 °C were observed for moisture cured AFUO films. This suggest that the crosslink between alkoxysilane domain and organic segment restricts the polymer motion. Therefore, the glass transition temperature of the moisture cured AFUO may become close to its decomposition temperature.

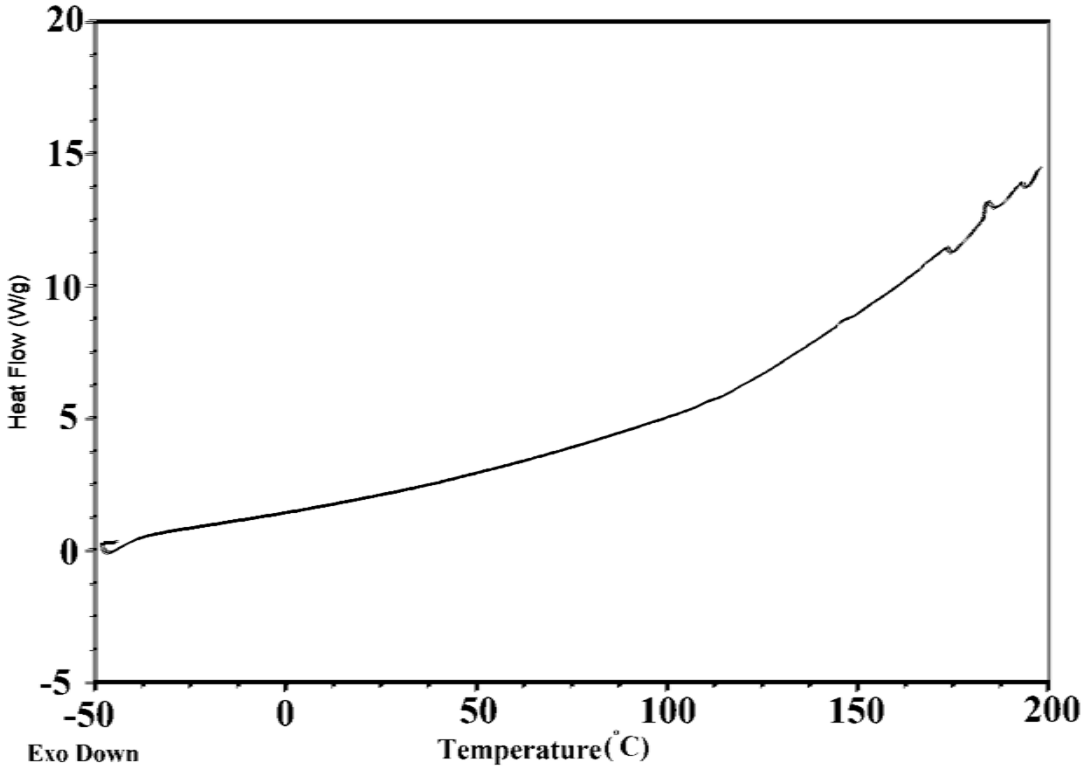


Figure 4.10 : DSC curve of moisture cured AFU

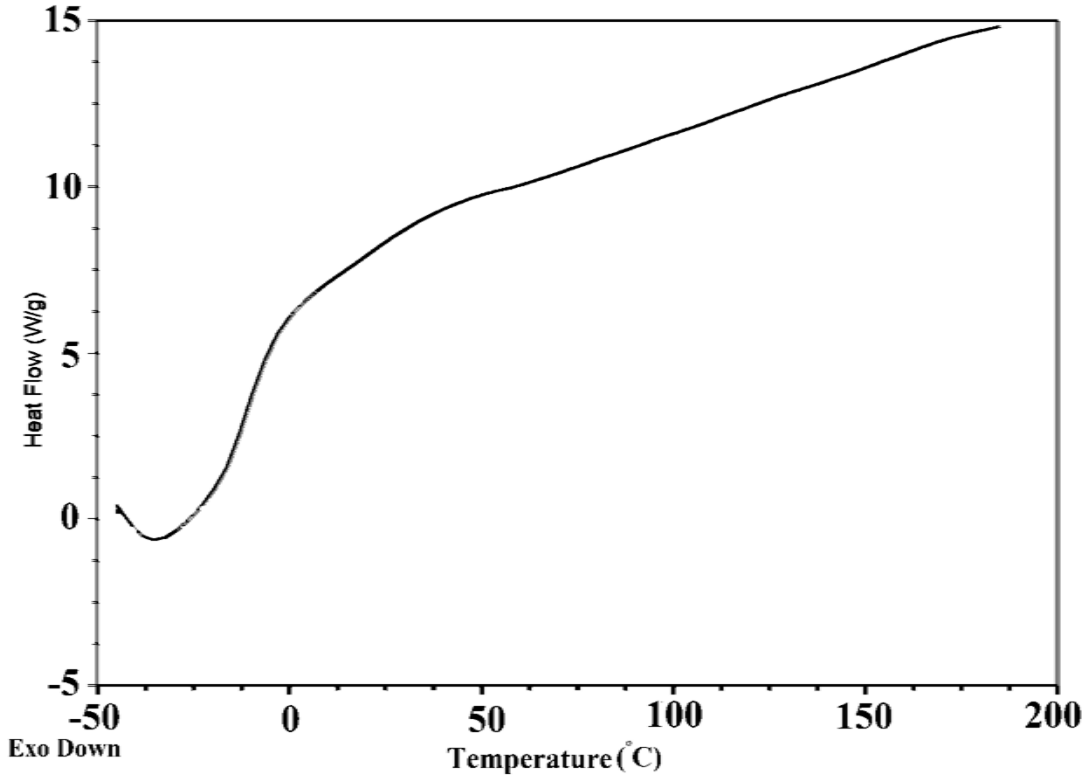


Figure 4.11 : DSC curve of air dried CUO

4.5.2 Differential scanning calorimeter of AFUO/titania hybrid films

Figure 4.12 shows DSC curves of AFUO/titania hybrid films prepared by using TIP in the range of 5-20 wt %. As seen, there is no detectable thermal transition temperature below 200 °C [6]. Since Si–O–Ti and Si–O–Si bonds restricts the polymer chain motion, the glass transition temperatures of the hybrid films may become close to their decomposition temperatures. Overall, DSC results prove that the covalent bonding occurs between inorganic and organic moieties, and the hybrid films exhibit good thermal stability.

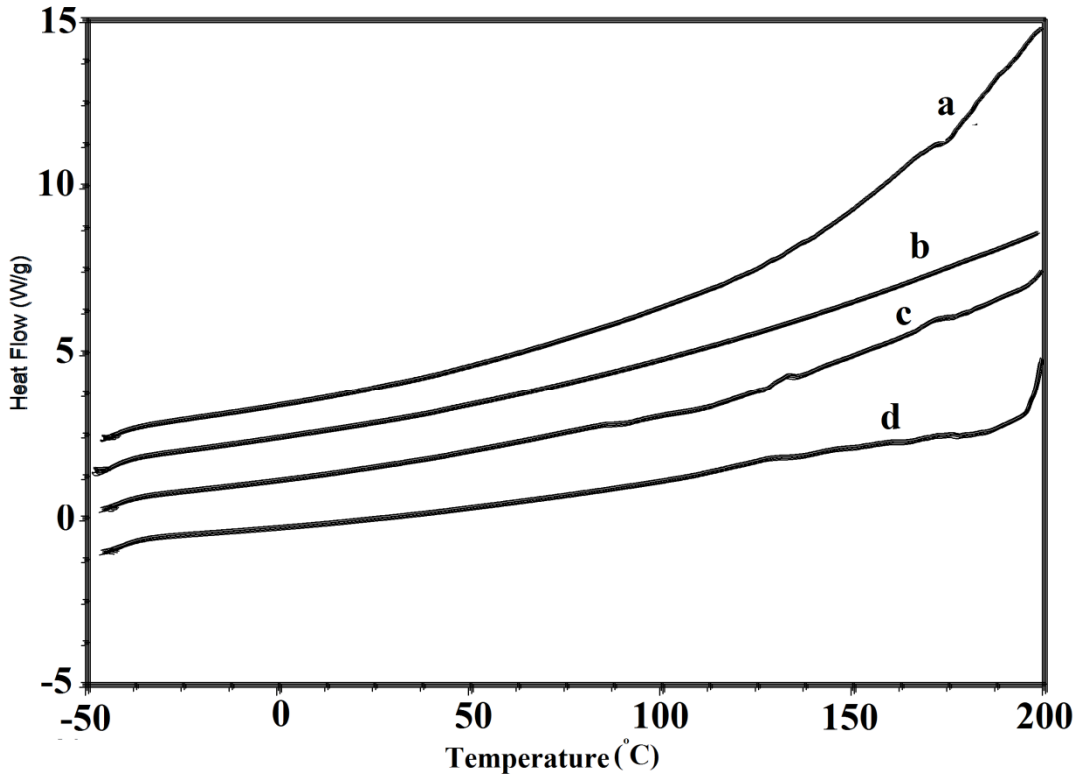


Figure 4.12 : DSC curves of AFUO/titania hybrid films prepared by using (a) 5, (b) 10, (c) 15 and (d) 20 wt % of TIP.

4.6 Film Properties

4.6.1. Film properties of moisture cured AFUO

Table 4.2 shows the film properties of AFUO and CUO. As seen, the expected improvements in adhesion, alkali resistance and water resistance were observed. Furthermore, AFUO and CUO samples showed no change in acid resistance test for the duration of 24 hours.

The enhancement of adhesion is due to the Si—O—Si bonding at the substrate interface as stated previously. Similar results in adhesion were also achieved by Soucek and his coworkers [46]. In their study, APES and hexamethylene diisocyanate (HDI) were reacted to prepare alkoxysilane functionalized isocyanurates and then obtained product was mixed with HDI to form a hybrid coating. It was reported that modifying HDI isocyanurate with alkoxysilane enhances the adhesion and increases the crosslink density.

In the present study, in addition to the enhancement of adhesion, AFUO samples exhibited better alkali resistance than CUO even without adding driers. Alkali resistance is the failure time of the films immersed into the alkali solution. Most probably due to higher crosslink density, alkali molecules cannot easily diffuse into the structure and the film damage time becomes longer. Regarding water resistance, while whitening disappeared within 30 min in case of CUO, AFUO samples showed no whitening. Moreover, harder films were produced by AFUO. It seems clear that higher crosslink density is also responsible for the better water resistance and harder films.

Film properties of AFUO without adding driers were determined as well. Although better properties were found in comparison with classical urethane oil, the films showed tacky property to some extent. This is an expected result since the crosslinking of the fatty portion by autoxidation cannot be completed without driers. This shows that in case of triglyceride oil based urethane oil, moisture curing alone cannot provide sufficient crosslinking for desired film properties. For that reason, driers should be added to ensure the autoxidation take place on the fatty acid portion.

Table 4.2 : Film properties of sunflower oil based CUO and AFUO with and without driers

	Applied Test							
Sample	Flexibility[a]	Adhesion[b] on a glass surface	Adhesion[b] on a tin plate	Hardness	Acid Resistance[c]	Alkali Resistance[d]	Water Resistance	Drying time
AFUO with driers	2 mm	5B	5B	12	no change	4 h	no visible affect	not available[e]
AFUO without driers	2 mm	5B	5B	4	no change	2 h	no visible affect	not available[e]
CUO	2 mm	4B	5B	8	no change	20min	30 min	80 min

[a]The diameter of cylinder which caused no crack on the film [23].
[b]The test method B was applied.
[c]The test was carried out at 25 °C with 9 % H_2SO_4 solution.
[d]The test was carried out at 25 °C with 3% NaOH solution.
[e]Film samples were subjected to moisture curing.

4.6.2. Film properties of AFUO/titania hybrid films

Film properties of AFUO/titania hybrid films prepared by using 5 to 20 wt. % of TIP were investigated (see Table 4.3). Samples of AFUO/titania hybrid films containing 25, 40 and 50 wt. % of TIP were also prepared but it was seen that the films were very brittle due to high portion of the inorganic domain. Therefore, the film properties of these samples could not be investigated.

As seen from Table 4.3, all the film samples exhibited good flexibility, adhesion, water and acid resistance. However, TiO_2-AFUO hybrid film, containing 20 wt % of titania showed higher resistance to alkali. These results suggest that AFUO/titania hybrid film with 20 wt % of titania gave the best film properties within the all AFUO/titania hybrid films.

Table 4.3 : Film properties of TiO_2-AFUO hybrid materials contain 5-20 wt.-% of titania

	Applied Test						
Sample (wt. % titania content)	Flexibility[a]	Adhesion[b] on a glass surface	Adhesion[b] on a tin plate	Hardness	Acid Resistance[c]	Alkali Resistance[d]	Water Resistance
5	2 mm	5B	5B	6	no change	2.5 h	no visible affect
10	2 mm	5B	5B	8	no change	3.5 h	no visible affect
15	2 mm	5B	5B	10	no change	4 h	no visible affect
20	2 mm	5B	5B	12	no change	7 h	no visible affect
25 and above[e]	–	–	–	–	–	–	–

[a]The diameter of cylinder which caused no crack on the film [23].
[b]Test method B was applied.
[c]Test was carried out at 25 °C with 9 % H_2SO_4 solution.
[d]Test was carried out at 25 °C with 3 % NaOH solution.
[e]no film formation on the surface due to high brittleness.

5. CONCLUSION

In conclusion, synthesis of AFUO/titania hybrid films were successfully achieved by sol-gel method. AFUO was firstly synthesized by the reaction of APES and partial gyceride mixture with TDI. Then, this intermediate was combined with TIP.

FTIR and DSC results indicated that the titania phase was incorporated into the urethane oil structure through Si–O–Ti bonding.

Both AFUO film samples and AFUO/titania hybrid films showed better film properties then CUO. Improvements in adhesion, alkali resistance and water resistance were observed for AFUO samples compare to CUO. Furthermore, AFUO /titania hybrid films prepared by using 5-20 wt. % of TIP showed good flexibility, adhesion, water and acid resistance. In case of alkali resistance, AFUO/titania hybrid film with 20 wt. % of TIP exhibited the highest alkali resistance with 7 h.

TGA analysis suggested that both AFUO and AFUO/titania hybrid films exhibited higher thermal stability then CUO due to their crosslink structure.

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